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THERMOPLASTIC POLYURETHANE RESIN FOR  
BREATHABLE AND WATERPROOF MATERIAL USE  
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## 1. Title

Thermoplastic Polyurethane Resin for Breathable and Waterproof Material Use

## 2. Claims

A thermoplastic polyurethane resin for breathable and waterproof material use that is characterized by the fact that its soft segment is comprised of 3 to 50 % by weight, based on the solid content of the thermoplastic polyurethane resin, of polysiloxane diol whose average molecular weight is in the range of 600 to 3,000, of polyoxy tetramethylene glycol having an average molecular weight in the range of 800 to 2,200 in a quantity that is 0.6 time or higher the content of the aforesaid polysiloxane diol, and, if necessary, of diols other than the aforesaid polysiloxane diol and polyoxy tetramethylene glycol, while its hard segment is comprised of aliphatic diisocyanate and aliphatic diamine.

## 3. Detailed Description of the Invention

## [Industrial Field of Application]

The present invention pertains to a novel and useful thermoplastic polyurethane resin for breathable and waterproof material use that has excellent breathable and waterproof properties. More specifically, it pertains to a thermoplastic polyurethane resin

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\* Number in the margin indicates pagination in the foreign text.

that is comprised of a specific soft segment and hard segment and that is suitably used for breathing and waterproofing processing material intended for various fields of industries, including the clothing industry, or for the medical field.

[Prior Art]

It is a common knowledge that clothing materials are required to have many properties, including breathability, light fastness, NO<sub>x</sub> resistance (oxidant resistance), surface smoothness, water repellency, suppleness, hydrolysis resistance, and washability. Of these, as sports wear is becoming more common, it has become essential for clothing materials to have both high breathability and an excellent waterproofing property.

To obtain highly breathable film, regardless of whether it is /142 polyurethane resin film or film of another synthetic resin, a commonly practiced method is to make the film porous or to impart hydrophilicity to the resin, instead of making the film porous.

[Problems that the Invention Intends to Solve]

When the method of making a film porous is employed, high breathability can be achieved, but, on the other hand, this processing method itself is relatively complex, and, furthermore, the obtained film cannot be made stronger easily and also is susceptible to water leakage, which fact then leads to the problem of a decrease in water resistance in washing.

Meanwhile, when the method of imparting hydrophilicity to a resin is employed, this process itself is not troublesome and also yields a film with high strength, but, on the other hand, this method has a disadvantage in that a high degree of breathability is difficult to obtain with this method and also in that imparting hydrophilicity to the resin causes the water resistance and hydrolysis resistance of the film proper to deteriorate easily.

Accordingly, as long as the conventionally practiced methods are employed, highly breathable film that is satisfactory cannot necessarily be obtained.

[Means of Solving the Problems]

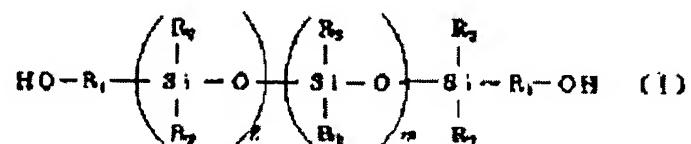
Therefore, the present inventors researched extensively to provide a urethane resin that can be prepared with a simple processing method, that is nonporous, thus posing no danger of water leakage, that has high breathability and, at the same time, high water repellency, and that achieves a balance in such properties as surface smoothness, light fastness, NO<sub>x</sub> resistance, water resistance, hydrolysis resistance, etc.; as a consequence, they learned that the presence of a specific soft segment, polysiloxane diol, makes it possible to realize the aforesaid objective, thereby attaining the present invention.

More specifically, the present invention intends to provide a thermoplastic polyurethane resin having high breathability and a

waterproofing property for breathable and waterproof material use whose soft segment is comprised of 3 to 50 % by weight, based on the solid content of the thermoplastic polyurethane resin, of polysiloxane diol whose average molecular weight is in the range of 600 to 3,000, of polyoxy tetramethylene glycol having an average molecular weight in the range of 800 to 2,200 in a quantity that is 0.6 time or higher the content of the aforesaid polysiloxane diol, and, if necessary, of diols other than the aforesaid polysiloxane diol and polyoxy tetramethylene glycol, while its hard segment is comprised of aliphatic diisocyanate and aliphatic diamine.

Here, the aforesaid polysiloxane diol indicates a compound represented by:

General Formula



(wherein  $\text{R}_1$  is an alkyl group having 1 to 6 carbon atoms;  $\text{R}_2$ , a methyl group or phenyl group; and  $\text{R}_3$ , a phenyl group or an alkyl group having 1 to 15 carbon atoms, while  $l$  and  $m$  are integers that set the average molecular weight of the polysiloxane diol to a range of 600 to 3,000.)

The content of said polysiloxane diol in the polyurethane resin of the present invention is preferably in the range of 3 to 50 % by weight, based on the weight of the solid content of the polyurethane resin of the present invention. If the content is less than 5 % by

weight, it becomes difficult to obtain satisfactory water resistance or surface smoothness, and a content exceeding 50 % by weight is also not desirable because the cost increases.

If the average molecular weight of said polysiloxane diol is less than 600, the water repellency and smoothness that are specific to silicone cannot be expected, whereas an average molecular weight /143 exceeding 3,000 causes deterioration of the miscibility of polysiloxane diol with the other urethane resin ingredients, that is, polyoxy tetramethylene glycol, diols other than said polysiloxane diol and polyoxy tetramethylene glycol, aliphatic diisocyanate, and aliphatic diamine, thus making it difficult to obtain a stable polyurethane resin solution and, in turn, making the resulting film less uniform. Therefore, neither range is preferable.

The content of the aforesaid polyoxy tetramethylene glycol in the polyurethane resin of the present invention must be 0.6 time or higher preferably in a range of 0.6 time to 5 times, the content of the aforesaid polysiloxane diol.

If the content of said polyoxy tetramethylene glycol becomes less than 0.6 time the content of the aforesaid polysiloxane diol, the miscibility with this polysiloxane diol decreases drastically, and, as a consequence, it becomes difficult to obtain uniform polyurethane resin film.

The average molecular weight of said polyoxy tetramethylene glycol is preferably in the range of 800 to 2,200. If it is less than 800 or, on the contrary, more than 2,200, the miscibility with the aforesaid polysiloxane diol decreases extremely, and, as a result, a stable resin solution cannot be obtained easily. Thus, neither range is desirable.

The aforesaid aliphatic diisocyanate includes a wide range of compounds that have two isocyanate groups in a molecule, each of said isocyanate groups not bonding directly with an aromatic ring. Of these compounds, some representative compounds include isophorone diisocyanate (IPDI), dicyclohexyl methane-4,4'-diisocyanate (hydrogenated MDI), hexamethylene diisocyanate (HDI), hydrogenated xylene diisocyanate (HXDI), etc. These may be used alone or in combination of two or more.

The aforesaid aliphatic diamine includes a wide range of compounds that have two amino groups in a molecule, each of said amino groups not bonding directly with an aromatic ring. Of these, some representative compounds include dicyclohexyl methane-4,4'-diamine (hydrogenated MDA), ethylene diamine, isophorone diamine (IPDA), hexamethylene diamine, etc.

Diols used in the preparation of the thermoplastic polyurethane resin of the present invention as the diols other than the aforesaid polysiloxane diol and polyoxy tetramethylene glycol may be any diols



that are commonly used in the production of polyurethane resins, and some representative examples include polyoxy alkylene glycols (polyoxy alkane diol), such as polyoxy ethylene glycol or polyoxy propylene glycol; compounds that have two alcoholic hydroxyl groups in one molecule, some examples of which include ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, neopentyl glycol, 3-methyl-1,5-pentane diol, or cyclohexane dimethanol (cyclohexane dimethylol); ester diols formed from these various glycols (diols) and succinic acid, adipic acid, azalea acid, sebacic acid, dibasic acids, such as phthalic acid, isophthalic acid, telephthalic acid, etc., carbonic acid, etc.; and diols obtained by ring-opening polymerization of  $\alpha$ -caprolactone.

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No specific limitation is imposed on the manner of formulating the thermoplastic polyurethane resin of the present invention from the various urethane resin ingredients described in the foregoing. With respect to the ratio of the hydroxyl groups of the long-chain diols, which comprise the soft segment, to the isocyanate groups of the aliphatic diisocyanate, 1/1.3 - 1/4.5 or thereabouts is suitable, and the use of what is called a prepolymer method is recommended here, according to which an isocyanate prepolymer is prepared in the aforesaid ratio and subsequently undergoes chain elongation with the use of aliphatic diamine.

This series of reactions is generally carried out in a solution. In this regard, from the viewpoint of the miscibility of the solvent with various diols (glycols), including polysiloxane diol, in the aforesaid urethane resin ingredients and of the miscibility, etc., with the obtained thermoplastic polyurethane resin, it is desirable to use, as the solvent, in an appropriate ratio, dimethyl formamide, independently or as a mixture with another solvent; a solvent mixture of toluene and alcohol, such as isopropanol, etc.; or a solvent mixture of toluene and glycol ether, such as ethyl cellosolve, etc.

For the thermoplastic polyurethane resin of the present invention, a reaction catalyst that is conventionally used may be used as necessary, and various commonly used kinds of additives, such as pigments, fillers, light stabilizers, antioxidants, etc., may also be incorporated as long as they do not adversely affect the objectives and effects of the present invention.

#### [Effects of the Invention]

Because the thus obtained thermoplastic polyurethane resin of the present invention for breathable and waterproof material use contains polysiloxane linkages in the molecules, the film obtained from the polyurethane resin of the present invention has not only excellent surface smoothness but also excellent water repellency, and it also exhibits high breathability as well as good light fastness,  $\text{NO}_x$  resistance, hydrolysis resistance, and washability, thus rendering

itself ideal especially as a breathing and waterproofing processing material.

[Working Examples]

The following explains the present invention in further detail, referring to working examples and comparative examples, and, unless otherwise stated, parts and % in the following are all based on weight.

Various physical properties of the obtained resin were evaluated according to the following methods.

Elongation strength comprised of 100 % modulus, breaking strength, elongation at rupture was evaluated as follows: a strip of film having a width of 5 mm and a marking-line interval of 20 mm was used as a sample, and it was aged for 3 days in a room at 20° C and 65 % relative humidity, after which elongation strength was measured in the same room at a pull speed of 300 mm/minute.

Breathability was determined according to JIS Z-0208. That is, using a circular film whose radius was 30 mm as a sample, the breathability of this sample was measured in an ambience of 40° C and 90 % relative humidity.

Surface smoothness was evaluated as follows. A film having a thickness of 20  $\mu$ m was formed on a glass substrate and used as a sample, and this sample was placed in a room at 20° C and 65 % relative humidity and aged for 3 days, after which the coefficient of friction was measured using "HEIDON-14" (a surface property tester

manufactured by Heidon Co., a West Germany company) under a load of 20 g to determine the surface smoothness.

With regard to water resistance, a water droplet was placed on a film, and the contact angle of this water droplet was measured with a goniometer. Meanwhile, a 5 cm x 5 cm size film was immersed in water for 10 minutes, after which the area swelling rate of the film was found. Thus, the water resistance of the film was evaluated based on the contact angle and water swelling rate.

Hydrolysis resistance was determined by measuring, in the same /145 manner as described before, the elongation strength of a film after it was kept in an ambience of 70° C and 95 % relative humidity for 4 days and by calculating the retention rate of the breaking strength from the value of this elongation strength.

Light fastness was evaluated as follows. Using "Shimazu Fade Tester CF-208" (a fade meter manufactured by Shimazu Seisakusho Co.), a sample was exposed to light for 100 hours in an ambience of 63° C and 40 % relative humidity and was subsequently aged for 3 days in a room that was maintained at 20° C and 65 % relative humidity, after which the elongation strength and degree of yellowing ( $\Delta N$ ) were measured to determine the light fastness.

No<sub>x</sub> resistance was evaluated according to JIS L-0855 (the old method) as follows: a film was exposed to an NO<sub>x</sub> gas (oxidant gas) at a double concentration for 6 hours and subsequently was dried for one

day and night, after which the degree of yellowing ( $\Delta N$ ) was measured to determine the resistance.

#### Working Example 1

Into a reaction container equipped with a stirrer, reflux condenser, and thermometer were charged 45 parts of polysiloxane diol (a product of Sin-Etsu Silicone Co. was used) whose average molecular weight was 2,000, 45 parts of polyoxy tetramethylene glycol (PTMG) whose average molecular weight was 2,000, 60 parts of poly(1,4-butane diol adipate) (PBA) whose average molecular weight was 2,000, and 50 parts of toluene to dissolve these components, to which solution 50 parts of IPDI and 0.05 part of dibutyl tin dilaurate as a reaction catalyst were subsequently added and reacted at 80° C for 4 hours. Then, 60 parts of toluene was added to the system, and the temperature was decreased to 50° C or below, thereby obtaining an isocyanate prepolymer solution whose isocyanate equivalent weight was 1,100.

Separately, into another reaction container equipped with a stirrer, reflux condenser, and thermometer were charged 25 parts of  $H_{12}$  MDA, 190 parts of toluene, 300 parts of isopropanol (IPA), 140 parts of methyl cellosolve, and 0.15 part of di-n-butyl amine (D-nBA) as a reaction terminator, and 270 parts of the isocyanate prepolymer solution was further added to this and reacted at 35° C for 2 hours, thereby obtaining a colorless and transparent polyurethane resin solution whose nonvolatile content (N. V.) was 20 % and whose

viscosity at 25° C (the same also applies in the following) was 14,000 cps.

#### Working Example 2

In this example, as the starting raw materials, 18 parts of polysiloxane diol whose average molecular weight was 2,000, 90 parts of PTMG whose average molecular weight was 2,000, 42 parts of poly(1,3-propylene glycol) (PPG) whose average molecular weight was 2,000, and 50 parts of toluene were used to form a solution. Except for this change, an isocyanate prepolymer solution whose isocyanate equivalent weight was 1,100 was prepared in the same manner as in Working Example 1.

The subsequent process was also carried out in the same manner as in Working Example 1, except that this isocyanate prepolymer solution was used, thereby obtaining a colorless and transparent polyurethane resin solution whose N. V. was 20 % and whose viscosity was 9,600 cps.

#### Working Example 3

In this example, as the starting raw materials, 90 parts of polysiloxane diol whose average molecular weight was 2,000, 60 parts of PTMG whose average molecular weight was 2,000, and 50 parts of toluene were used to form a solution. Except for this change, an isocyanate prepolymer solution whose isocyanate equivalent weight was 1,100 was prepared in the same manner as in Working Example 1.

The subsequent process was also carried out in the same manner as in Working Example 1, except that this isocyanate prepolymer solution was used, thereby obtaining a colorless and transparent polyurethane resin solution whose N. V. was 20 % and whose viscosity was 13,500 cps.

#### Working Example 4

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In this example, as the starting raw materials, 45 parts of polysiloxane diol whose average molecular weight was 2,000, 45 parts of PTMG whose average molecular weight was 2,000, 45 parts of polyethylene glycol (PEG) whose average molecular weight was 2,000, and 50 parts of toluene were used to form a solution. Except for this change, an isocyanate prepolymer solution whose isocyanate equivalent weight was 1,100 was prepared in the same manner as in Working Example 1.

The subsequent process was also carried out in the same manner as in Working Example 1, except that this isocyanate prepolymer solution was used, thereby obtaining a polyurethane resin solution whose N. V. was 20 % and whose viscosity was 9,100 cps.

#### Working Example 5

In this example, as the starting raw materials, 45 parts of polysiloxane diol whose average molecular weight was 1,000, 60 parts of PTMG whose average molecular weight was 1,000, 45 parts of PEG whose molecular weight was 2,000, and 55 parts of toluene were used to form a solution. Next, the quantity of IPDI to be added was changed to

60 parts and also the quantity of toluene to be added was changed to 85 parts. Except for these changes, an isocyanate prepolymer solution whose isocyanate equivalent weight was 1,225 was prepared in the same manner as in Working Example 1.

The subsequent process was also carried out in the same manner as in Working Example 1, except that the quantities of H<sub>12</sub> MDA, toluene, IPA, methyl cellosolve, and D-nBA were changed to 20 parts, 130 parts, 225 parts, 110 parts, and 0.12 part, respectively, and that the quantity of the isocyanate prepolymer solution to be added was also changed to 242 parts, thereby obtaining a colorless and transparent polyurethane resin solution whose N. V. was 20 % and whose viscosity was 15,000 cps.

#### Comparative Example 1

In this comparative example, as the starting raw materials, 105 parts of PTMG whose average molecular weight was 2,000, 45 parts of PBA whose average molecular weight was 2,000, and 50 parts of toluene were used to form a solution. Except for this change, a comparative-example isocyanate prepolymer solution whose isocyanate equivalent weight was 1,100 was prepared in the same manner as in Working Example 1.

The subsequent process was also carried out in the same manner as in Working Example 1, except that this comparative-example isocyanate prepolymer solution was used, thereby obtaining a comparative-example



polyurethane resin solution. It was a colorless and transparent solution whose N. V. was 20 % and whose viscosity was 12,100 cps.

#### Comparative Example 2

In this comparative example, as the starting raw materials, 60 parts of PTMG whose average molecular weight was 2,000, 45 parts of PEG whose average molecular weight was 2,000, 45 parts of PBA whose average molecular weight was 2,000, and 50 parts of toluene were used to form a solution. Except for this change, a comparative-example isocyanate prepolymer solution whose isocyanate equivalent weight was 1,100 was prepared in the same manner as in Working Example 1.

The subsequent process was also carried out in the same manner as in Working Example 1, except that this comparative-example isocyanate prepolymer solution was used, thereby obtaining a comparative-example polyurethane resin solution. It was a colorless and transparent solution whose N. V. was 20 % and whose viscosity was 12,700 cps.

#### Comparative Example 3

In this comparative example, as the starting raw materials, 45 parts of polysiloxane diol whose average molecular weight was 2,000, 18 parts of PTMG whose average molecular weight was 2,000, 87 parts of PBA whose average molecular weight was 2,000, and 50 parts of toluene were used to form a solution. Except for this change, a comparative-example isocyanate prepolymer solution whose isocyanate equivalent weight was 1,100 was prepared in the same manner as in Working

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Example 1.

The subsequent process was also carried out in the same manner as in Working Example 1, except that this comparative-example isocyanate prepolymer solution was used, thereby obtaining a comparative-example polyurethane resin solution. It was a somewhat opaque solution whose N. V. was 20 % and whose viscosity was 10,500 cps.

Moreover, the film obtained from this resin solution according to a commonly practiced method was also opaque, and separation took place in this resin solution itself three days later.

The resins thus obtained in the aforesaid working examples and comparative examples were compared and evaluated for the physical properties of the films formed from them. The results are summarized and shown in Table 1.

TABLE 1

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Content (%)	Polysiloxane Diol PTMG	Working Examples					Comparative Example		
		1	2	3	4	5	1	2	3
Physical Property	100 % Modulus (kg/cm <sup>2</sup> )	20	8	40	20	20	-	-	20
	Breaking Strength (kg/cm <sup>2</sup> )	20	40	27	27	27	47	27	8
	Elongation Strength	60	60	65	60	70	70	70	55
	Elongation at Rupture (%)	400	360	380	420	480	300	450	150
Physical Property	Breathability (g/m <sup>2</sup> /24 hrs.)	400	450	430	420	400	450	400	200
	Coefficient of Friction	3200	3000	3500	4600	4300	1200	3000	2800
	Water Resistance	0.2	0.3	0.1	0.2	0.2	2.4	2.5	0.8
	Water Swelling Rate %	0					5	64	0
	Contact Angle (degree)	100	97	99	97	98	78	70	97
	Hydrolysis Resistance [Breaking Strength Retention Rate (%)	60	50	55	45	50	30	10	50
Physical Property	NO <sub>x</sub> Resistance (AN)	1.8	1.6	1.3	1.7	1.5	2.0	2.0	1.7
	Light fastness [Breaking Strength Retention Rate (%)	72	65	80	65	70	50	40	65

As shown in Working Examples 1 through 5, the thermoplastic polyurethane resins of the present invention were strong and had excellent breathability. It can also be seen that these resins had hydrophobicity that caused the contact angle with water to exceed 90 degrees.

As in Working Examples 4 and 5, when a hydrophilic PEG, for example, was copolymerized, breathability was further improved and, without swelling with water, the film exhibited a contact angle that exceeded far beyond 90 degrees, which indicated that hydrophobicity was still retained, and this fact merits attention.

It goes without saying that the thermoplastic polyurethane resins of the present invention also had excellent hydrolysis resistance, weather resistance, NO<sub>x</sub> resistance, etc.

On the other hand, as shown in Comparative Example 1, a polyurethane resin for which no polysiloxane diol was used at all had inferior breathability and poor surface smoothness as well as inferior hydrolysis resistance and weather resistance. As can be seen from Comparative Example 2, when no polysiloxane diol was used at all but hydrophilic PEG was copolymerized, breathability was improved, but imparting hydrophilicity to the resin in this manner leads to further deterioration of hydrophobicity, which was defined by a water swelling rate, contact angle, etc., and hydrolysis resistance was also extremely poor.

As shown in Comparative Example 3, with respect to a polyurethane resin whose polysiloxane diol content was less than 0.6 time the content of PTMG, the resin proper became opaque, and the storage stability of the resin solution also deteriorated.